Greenfield.

Base Replaceibility Of Certain Clays And Their Applicability To Water Softening.

BASE REPLACEIBILITY OF CERTAIN CLAYS AND THEIR APPLICABILITY TO WATER SOFTENING

BY

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BASE REPLACEABILITY OF CERTAIN CLAYS
AND THEIR APPLICABILITY TO
WATER SOFTENING.

Introduction.

Certain silicates containing aluminium when acted upon by salt solutions have the property of exchanging their base forming elements for those present in greater molecular proportions in the salt solution. Until quite recently very little scientific investigation has been made of the mechanism of this reaction. In fact at the present time the views on this subject are very conflicting. There are several well known facts that all will admit and which must be incorporated in any theory. The original silicate and that resulting from the action of the salt solution are practically insoluble in water. The transfer of bases is in some cases quite rapid. The transfer will proceed in either direction, depending upon the concentration of the bases in the solution.

One explanation of the reaction is that the silicate is slightly soluble in water, that it is ionised in the solution like any salt, and that this is an ionic reaction. For example let us represent a silicate in which sodium

is the base by Na_2X. The following equilibrium equation represents the condition when it is suspended in pure water.

$$(1)\ Na_2X \leftrightharpoons 2\ Na^+ + X^{--}$$

If now we take instead of pure water a solution of calcium chloride we must add two more equilibrium equations in addition to the one above before we describe all the conditions.

$$(2)\ CaCl_2 \leftrightharpoons Ca^{++} + 2\ Cl^-$$

$$(3)\ Ca^{++} + X^{--} \leftrightharpoons CaX$$

If the concentration of the calcium ions is greater than can be in equilibrium with the concentration of the X ions furnished by the solution of the Na_2X, CaX will be precipated and this precipitation will continue until the two equilibria are adjusted to each other. This solution of Na_2X and precipitation of CaX bring about the transference that we observe to take place. This can be represented by the following equation.

$$(4)\ Na_2X + CaCl_2 \leftrightharpoons CaX + 2\ NaCl$$

This equation is simply a summation of (1) and (3) and is an equilibrium reaction. The reaction actually will take place in either direction which also shows that it is an equilibrium reaction.

Another explanation of the reaction offered by C.

Wiegner[39] is that the aluminium silicate consists of colloidal particles which have films of water between them. These particles absorb negative hydroxyl ions, and the corresponding positive ions, for example sodium ions, are free in the water surrounding the particles, but are held from wandering away by the charge of the adsorbed negative ion.

The transference is simply the entrance to the sphere of influence of other positive ions, for example calcium ions, and the expulsion of the original positive ions.

Composition of the Base Replacing Silicates.

Of the silicates having this base transfering power the zèolites have been the most studied. Zeolites are silicates of aluminium usually with sodium and calcium, as for example analcime, chabasite, stilbite, etc.[36] The are found in nature[6] in cavities and veins in basic igneous rocks and less frequently in granite and gneiss, etc.

Dr. Gans[36] has divided the aluminium zeolites into two classes. Viz; (1) double earthy silicates--zeolites which contain the alkaline earths and alkalies mostly combined with the silicic acid. The bases in these zeolites are replaced very slowly; (2) aluminate silicates--zeolites which contain the alkaline earths and alkalies combined with

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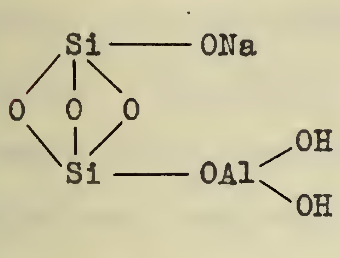
the aluminate radicle. The bases in this class of zeolites are replaced quite readily.

As an example of the first class we might give analcime[8], which has the formula $Na_2Al_2Si_4O_{12}.2H_2O$, represented graphically as follows,-



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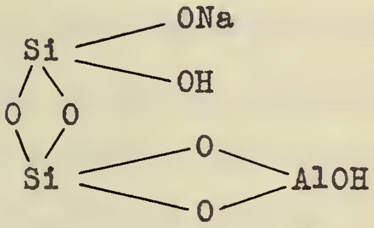
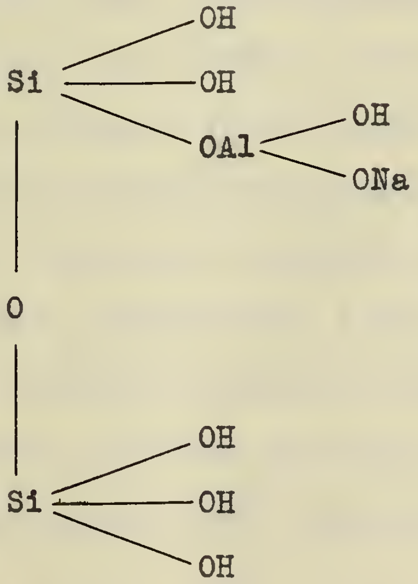


As an example of the second class we might give chabasite[8], which has the formula $Na_2Al_2Si_4O_{12}.6H_2O$ represented graphically as follows,-



Permutit an artificial product is of the second class.

A considerable amount of experimental work has been

done[29,30] on aluminium silicates of the type $RO.Al_2O_3.n\ SiO_2.mH_2O$ in which R is some element of the alkaline earth of alkali metals groups. "n" is a coefficient varying with the nature of the silicate. "m" is also a coefficient varying with the nature of the silicate. The experiments were carried on by treating the silicates with various salt solutions at and above the temperature of boiling water until all action had ceased. The period necessary to obtain complete equilibrium varied from a few hours to a year and a half. The undissolved substance remaining was analyzed in every case, but no analysis of the soluble material is reported. The element R of the original compound could be replaced completely by a similar element of the salt in the solution. At the same time the coefficient "m" might change its value apparently being a function of the base being introduced. The coefficient "n" also varied. In case the acting solution contained a carbonate, chloride, sulphate, or hydroxide "n" became equal to two. If the acting solution contained a silicate "n" became equal to five. In case a compound of the type, $Al_2O_3.n\ SiO_2.m\ H_2O$ were treated with a salt solution for a sufficient length of time a compound of the type, $R\ O.\ Al_2O_3.n\ SiO_2.m\ H_2O$ resulted in every case. The quantities "n","m" varying in accordance with the principles outlined above.

The difference in the base replaceability between various silicates is simply one of speed of reaction rather

than one of completemess of reaction. If the silicate originally contains no base it will absorb one from the salt solution until the base constituent and the aluminium are in molecular proportions. According to Schneiderhöhn[39] the compound formed in this way has the power of exchanging the absorbed base for another, he does not say how rapidly this exchange will take place.

Very few experiments to show the practical application of the base replacing powers of natural silicates have been reported. Much work has been done to develop artificial compounds. Gans[11] has experimented with natural zeolites and reports that they contain too much inactive material to make them a practical substance for use in water softening devices. Thresh[33] reports that Mountsorrel granite and Thanit sand show base replacing power. This Thanet sand forms a rather important water-bearing stratum in England. The water from this stratum is soft but contains considerable quantities of sodium salts. Thresh advances the theory that this water originally contained salts of calcium and magnesium but that these have been converted to sodium salts by the passage through this sand. The reactivity of the sand was not sufficient to make its use in artifically softening of water practical. It was not pure silica but contained considerable quantities of aluminium and alkali metals. Probably the active part of the sand was an alumino-silicate. Kinniard[21] reports some water softening

experiments with a

clay from North Dakota. He reports this material to be very efficient. The clay is number 6 in the table.

Experiments with a Product of Natural Clay from the Black Hills.

These experiments are of a similar nature though not directly connected to the other experiments of the paper. One series of experiments was conducted to compare the artificial product permutit and the natural product when used in softening water. University of Illinois water was passed through two rather small filters, filled with permutit and the natural product respectively, at a rate that had proved to be optimum for the filters during previous experiments. The hardness was tested hourly by soap titration and a composite sample for mineral analysis collected hourly. The filtration was stopped as soon as water with a hardness equivalent to 30 parts per million calcium carbonate appeared. The results were as follows,-

Test of the Natural Product.

Weight of natural product.	9.45 kilo or 21 lbs.
Water softened.	556 liters, 146 gallons.
Time.	11 1/4 hours.

Analysis of Composite Samples of Raw and Treated Water.

Collected hourly, results in parts per million.

		Raw water	Treated water.
Calcium	Ca	78.6	6.36
Magnesium	Mg	31.9	3.3
Sodium	Na	26.8	137.1

Total calcium removed from water 40 grams.

Total magnesium removed from water 15.9 grams.

Total calcium as calcium oxide expressed in per cent total substance .59

Total magnesium as magnesium oxide expressed in per cent total substance .28

Sodium oxide equivalent of calcium oxide and magnesium oxide per cent total substance 1.08

Sodium oxide recovered from water as per cent of total substance .88

Analysis of Substance.

Regenerated		Exhausted.
7.37	H_2O below 130°C	11.85
4.63	H_2O above 130°C	3.73
55.52	SiO_2	55.78 & ins.
4.00	Fe_2O_3	3.62
21.24	Al_2O_3	18.04 See above
2.14	CaO	2.96
4.53	MgO	4.58
1.10	Na_2O	.29
.12	K_2O	.08
100.65	Total	100.93

Increase in CaO .82
Increase in MgO .05
Na_2O Equiv. of CaO & MgO .98
Na_2O Decrease .91

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Test of Permutit.

Weight of Permutit in filter 21 Kilos or 46.2 lbs. Calculated on air dried basis.

Water softened 2,550 liters, 675 gallons. Time 23 1/2 hrs.

Analysis of Composite Sample of Raw and Treated Water.

Collected hourly, results in parts per million.

		raw water	treated water.
Calcium	Ca	78.6	1.8
Magnesium	Mg	31.9	1.7
Sodium	Na	26.8	137.1

Total Calcium removed	195.4 grams.
Total magnesium removed	79.1 grams.
Total calcium removed as calcium oxide expressed as % total substance	1.30
Total magnesium removed as magnesium oxide expressed as % total substance	.63
Sodium oxide equivalent of calcium oxide and magnesium as % total substance	2.21
Sodium oxide recovered from water as % total substance	1.80

Analysis of Permutit.

Regenerated		Exhausted.
16.11	H_2O below 130°C	17.33
4.95	H_2O above 130°C	4.90
42.34	SiO_2	41.36
26.40	Fe_2O_3 & Al_2O_3	25.70
4.26	CaO	4.88
1.08	MgO	1.90
4.74	Na_2O	2.33
.34	K_2O	.60
100.22	Total	99.00

Increase in CaO	.62	
Increase in MgO	.82	
Na_2O equiv. of MgO & CaO		1.96
Na_2O decrease	2.41	

These results show that pound for pound the permutit is more reactive. If the two materials were of the same specific gravity this would mean that in order that a filter containing this product should do the same work as one containing permutit it would have to be larger. The natural product actually has a greater specific gravity than the permutit so this increased size of the filter would not be as much as the results would indicate. It would seem therefore that if the natural product could be produced enough cheaper

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to compensate for the necessary increased size of the filter that it would be able to compete with the artificial product.

Another sample of this same natural product did not show the reactivity that the first one did. Upon chemical examination it was found when air dried to contain only about 4.5 per cent moisture while the first sample contained about 13 per cent. Five hundred grams of the second sample would soften only from one to three liters of the University Water. This sample was treated with a 25 per cent salt solution under a pressure of twenty five pounds of steam for one hour. After this treatment it would soften from six to eight liters of water per five hundred grams of material. The water content was increased to 6 per cent. This shows that when these materials are dehydrated below a certain point that their reactivity becomes a direct function of their degree of hydration.

Experimental.

The purpose of the experiments was to measure the base replaceability of various clays, to find out first, if any had this property to an extent great enough to make their use in water softening practical, and second, if the clays in their original state did not have sufficient base replaceability to see if their power could be increased by treatment with the proper chemicals to make them of practical

use.

Samples of clay were obtained from the Ceramics Department of the University of Illinois, and from various other sources.

Methods Used.

In general a sample of the clay was treated with a strong solution of some sodium salt, the solution washed off and the residue treated with a measured amount of a standard calcium chloride solution. An analysis of the solution of calcium chloride gave the amount of calcium that had been absorbed.

Procedure.

Ten grams of the coarsely ground clay was treated with twenty-five cubic centimeters of a twenty per cent solution of sodium chloride or sodium hydroxide. In series 1 the sodium chloride was allowed to act over night at room temperature, in series 2 it was allowed to act for three quarters of an hour under a pressure of fifteen pounds of steam. In series 3 sodium hydroxide was allowed to act over night at room temperature. After the digestion the clays were washed by decantation until they would no longer settle readily, a little more sodium chloride was added and the washing continued until turbidity again resulted. Twenty-five cubic centimeters of a calcium chloride solution made by dissolving nine grams of calcium chloride in a liter, were added and the residue washed twice by decantation. The

washings containing calcium chloride were collected in a liter volumetric flask. Fifty cc. of the calcium chloride solution was then added and allowed to act over night. Washing by decantation was repeated and the wash water collected in the same liter flask. When a colloidal solution resulted the operation was finished by filtering and washing through a Berkefield filter, until calcium could no longer be detected in the wash water. The combined washings were made up to a liter and two hundred cubic centimeters taken for analysis. The calcium was precipitated with ammonium oxalate, filtered, washed, dissolved in dilute sulfuric acid, and titrated with tenth normal potassium permanganate. The original strength of the calcium chloride solution was obtained by diluting seventy-five cc. to a liter and determining the calcium in two hundred cc. The difference between the calcium in the original solution and in the washings from the clay is the amount of calcium absorbed by the clay,with the amounts used a difference of one cubic centimeter of tenth normal potassium permanganate is equivalent to fourteen hundredths (0.14) per cent calcium oxide taken up by the clay. This factor is sufficiently low to make the effect of the ordinary errors in titration negligible.

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Table showing the per cent of Calcium Oxide absorbed by the clays after treatment with sodium salts.

Series no.	Name of Clay	NaCl solution cold	NaCl solution steam 15lbs.	NaOH solution cold.
1	Urbana,Basement New Ceramics Bldg.	0.42	0.55	0.50
2	Canadian Clay	0.08		0.00
3	Grandville Clay	0.17		
4		0.56		0.66
5	Potash Feldspar	0.01		0.07
6	Clay from Black Hills	1.76	1.84	
7	Valentine New Jersey Fire Clay	0.14		0.28
8	White Hall Stone Ware	0.43	0.62	0.29
9	Mt. Savage #2 Fire Clay	0.10		0.11
10	Hobson Walker	0.27		0.25
11	Kentucky Pot Clay	0.18	0.15	0.43
12	Anna, Ill., Fire Clay	0.43		0.39
13	St. Louis Fire Clay	0.50	0.45	0.48
14	Streator Shale	0.28		0.27
15	Lasalle Shale	0.52		0.38
16	Ball Shale	0.27		0.11
17	GaKaolin	0.15		0.04
18	English China Clay	0.04	0.03	0.18
19	Hocheson Kaolin, N.J.	0.04		0.14
20	North Caroline Kaolin	0.08		0.15

Table Continued.

Series No.	Name of Clay.	NaCl solution cold	NaCl solution steam 15 lbs.	NaOH solution cold
21	Florida Kaolin	0.10		0.46
22	Tennessee Ball #7	0.22		0.28
23	English Ball #20	0.18		0.53
24	Halloysite	0.15	0.11	
25	Aluminium bearing Mineral from Kentucky	0.11	0.07	

Of these twenty-five clays only one possessed the property of base replaceability to any marked degree. This is the clay from the Black Hills and is the one used by Kinnaird in his water softening experiments. This clay was analysed with the following results,-

SiO_2	Silicon dioxide.	50.69
Fe_2O_3	Iron oxide.	2.68
Al_2O_3	Aluminium oxide	18.48
CaO	Calcium oxide.	3.43
MgO	Magnesium oxide	3.67
Na_2O	Sodium oxide	.39
K_2O	Potassium.	.17
	Loss on ignition.	21.42
	Total.	100.97

If we represent all the calcium, magnesium, sodium, and potassium by R", and if we disregard the iron as not being part of the compound this clay might be given the formula $R''O \cdot Al_2O_3 \cdot 6\ SiO_2 \cdot 7\ H_2O$. Of the elements represented by R" only twenty per cent are replaceable under the conditions of the experiments. Experimental work published by F. Singer[32] shows that a replaceability of about thirty per cent of the bases present is all that can be obtained with the best artificial zeolite that he was able to prepare. This compound had the formula $Na_2O \cdot Al_2O_3 \cdot 5\ SiO_2 \cdot 4\ H_2O$. Other quite reactive compounds prepared by him varied in SiO_2 content from three to seven. In every compound that he prepared the basic oxide and the aluminium oxide were in molecular proportions. It would seem therefore that this natural clay had about the optimum constitution and that it was about as reactive as we could expect it to be.

Of the other clays numbers 1, 4, 8, 12, 13, and 15, a replaceability greater than .4 per cent calcium oxide absorbed. These give practically the same results when treated with sodium hydroxide as when treated with sodium chloride. For the most part the clays responded equally well to the three methods of treatment. Three rather marked exceptions to this are seen in numbers 11, 21, and 23 where the calcium absorbtion was considerably greater after the treatment with sodium hydroxide.

Conclusions.

These results show that many clays in their natural state have very little power of base replaceability. The clay from Dakota is a marked exception. In some cases the replaceability may be increased by treatment with sodium hydroxide instead of sodium chloride. This increase has not been sufficient to make the resulting product of any practical value.

The results obtained with the Dakota clay and from data in the literature available on prepared zeolites it is evident that the reactivity of the clay from the Black Hills is nearly as high as that of the best prepared products.

Suggestions for Further Study.

It seems desirable to study the effect of sodium hydroxide at higher temperature upon those clays which show an increased reactivity upon being treated with a hydroxide at room temperatures. Those clays which show any reactivity should be analyzed and an attempt made to increase the reactivity by the introduction of constituents in which they seem to be lacking. A comparison should be made with the best artificial zeolites.

Acknowledgment.

The writer wishes to acknowledge the kindly interest in the progress of this work shown by Messrs. Langelier, Mohlman, and Bennett of the Illinois State Water Survey; to thank Mr. B. S. Radcliffe of the Ceramics Department of the University, and Mr. Gardner of Bedford, Indiana for the samples of clay they furnished, and to thank Dr. Edward Bartow for suggesting the topic and for the valuable suggestions made throughout the work.

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Compound for Purifying Water. Carl W. Schultze to The Clarne Co. 935,695. October 5, 1909.

Method of Purifying Water. Thomas Jones. 773,395. October 25, 1904.